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(54) **TREATMENT OF GAS CONTAINING FLUORINE COMPOUND**

(57)Abstract:

PROBLEM TO BE SOLVED: To decompose gas containing fluorine compounds efficiently at low temperatures by contacting a gas flow containing at least one of a compound consisting of two or more carbon atoms and fluorine atoms and a compound consisting of nitrogen atoms and fluorine atoms with a specified fluorine compound decomposition catalyst in the presence of water vapor.

SOLUTION: When implemented in the plasma CVD apparatus-cleaning process of a semiconductor production process, cleaning gas containing C₂F₆ 1 which was used for removing SiO₂ is sent into a CVD chamber and exited by plasma to remove SiO₂. After that, the chamber is replaced with N₂ 2, C₂F₆ concentration is reduced to about 3-5%, and gas is discharged. Reaction gas 5 in which the exhaust gas is added with air 3 and water vapor 4 is sent to a

decomposition process, in which the gas 5 is contacted with an Al₂O₃ catalyst at 400-800°C. Next, decomposition gas 6 is sent to an exhaust gas washing process, in which an alkali aqueous solution is sprayed, and exhaust gas 7 in which acid component in the decomposition gas 6 is eliminated is released outside the system.

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CLAIMS

[Claim(s)]

[Claim 1] The art of the fluorine compound content gas characterize by come to contain the process which the gas stream containing either [at least] the compound containing a fluorine atom or the compound containing a nitrogen atom and a fluorine atom be contact under existence of the steam of an effective dose at the catalyst of an alumina , a titania , a silica , and a zirconia which contain a kind at least , and the temperature of about 400-800 degrees C , and convert F in said gas stream into HF , include two or more carbon .

[Claim 2] The art of the fluorine compound content gas characterized by said fluorine compound content gas being the compound of C and F containing two or more carbon, or the compound of N and F in an approach according to claim 1.

[Claim 3] The art of the fluorine compound content gas by which said catalyst is characterized by including at least 1 component of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, and the nickel further in an approach according to claim 1.

[Claim 4] The fluorine compound decomposition catalyst which is a catalyst which processes the gas stream which contains at least one side for the compound of C and F containing two or more carbon, or the compound of N and F, and is characterized by for an alumina being less than [more than 75wt%98wt%], and a titania being more than less than [25wt%] 2wt% including an alumina and a titania.

[Claim 5] The fluorine compound decomposition catalyst characterized by including at least 1 component of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, nickel, P, and the B further in a catalyst according to claim 4.

[Claim 6] The fluorine compound decomposition catalyst characterized by including the oxide of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, nickel, P, and B at 0.1wt% - 10wt% to the amount of alumina titania catalyst main in a catalyst according to claim 5.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the decomposition art and catalyst ingredient which decompose efficiently fluorine compound content gas, such as C2F6, at low temperature.

[0002]

[Description of the Prior Art] Fluorine compound gas, such as C2F6, is used by the large quantity for a semi-conductor etching ingredient and semi-conductor washing. However, if these matter is emitted into atmospheric air, it has turned out that it is the quality of a warm ghost which causes warming of the earth. From now on, it will be expected to the processing after the activity of these compounds that severe regulation is performed.

[0003] By the way, gas, such as C2F6, contains many fluorines (F) as a molecule constituent. Electronegativity of a fluorine is the largest of all elements, and it forms the chemical very stable matter. C2F6 etc. have the especially strong intramolecular force, and it is the matter lacking in reactivity. From this property, an elevated temperature is required to decompose and the energy of a large quantity is consumed. Moreover, the decomposition reaction in an elevated temperature has the large corrosion rate of the equipment ingredient by gas, such as hydrogen fluoride to generate, and the actual condition is that there is no suitable decomposition art.

[0004] As a decomposition art, current and being proposed are the combustion technologies in an elevated temperature. However, by this approach, in order to use the fuel of a large quantity, energy efficiency is low and the problem of breakage on the furnace wall by the halogenated compound 1000 degrees C or more generated with combustion also has it. Therefore, the technique which can be decomposed more at low temperature is required.

[0005] About the catalyst, TiO2-WO3 catalyst is reported to JP,6-59388,B as a catalyst for decomposition of an organic halogenated compound until now. This catalyst is 0.1 - 20wt% of TiO2. It is a catalyst (when it is made an atomic ratio, Ti is 99.96% or less 92% or more, and W is 0.04% or more 8% or less) containing W, and although CCl4 of ppm order is processed, 99% of cracking severity was held at 375 degrees C for 1500 hours. Not only Cl but the F of the effect as catalyst poison is larger rather in an organic halogenated compound. With this official report, it is the organic halogenated compound 4 of a carbon number 1, i.e., CF. Although Cl2F2 grade can be decomposed, there is no example of the decomposition result about a fluorine compound. Moreover, generally compared with disassembly of the organic halogenated compound of a carbon number 1, it is hard to disassemble the organic halogenated compound of a carbon number 2. As another example, aluminum2O3-ZrO2-WO3 catalyst is reported to JP,7-80303,A as a decomposition catalyst of fluorine compound gas. This catalyst is a catalyst which understands chlorofluocarbon a burned part, carried out the combustion decomposition reaction to processing chlorofluocarbon -115 (C2ClF5) at 600 degrees C, and held 98% of cracking severity for 10 hours. Processing cost becomes large in order that this approach may add hydrocarbons, such as n-butane, as a combustion assistant. Moreover, although disassembly of the compound of only the carbon of C2F6 grade and a fluorine is still more difficult compared with chlorofluocarbon -115, there is no example of the decomposition result about these matter.

[0006]

[Problem(s) to be Solved by the Invention] The object of this invention offers the approach and catalyst which carry out decomposition processing of the gas containing either [at least] the compound containing a fluorine atom, or the compound containing a nitrogen atom and a fluorine atom efficiently at low temperature including two or more carbon.

[0007]

[Means for Solving the Problem] this invention persons were low temperature, and could be efficient, could decompose fluorine compound content gas, and as a result of advancing examination of the decomposition art which corrosion of the equipment by the hydrogen fluoride which moreover separates as a decomposition product cannot produce easily to a detail, they resulted in this invention.

[0008] That is, it found out that the fluorine in a gas stream could be converted into HF by contacting the gas stream containing either [at least] the compound containing a fluorine atom, or the compound containing a nitrogen atom and a fluorine atom under existence of the steam of an effective dose at a specific fluorine compound decomposition catalyst and the temperature of about 400 - 800 degrees C of abbreviation, including two or more carbon. As a decomposition catalyst, the catalyst of an alumina, a titania, a silica, and a zirconia which contains a kind at least can be used.

[0009] as a fluorine compound -- C2F6 etc. -- like -- a carbon number -- two or more compounds of C and F, and NF3 etc. -- there is a compound of N and F etc.

[0010] Furthermore, when at least 1 component of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, and the nickel was added for the catalyst, it found out that fluorine compound content gas could be decomposed in higher activity. These catalysts contain the oxide of an alumina, a titania, a silica, a zirconia, and at least 1 component of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, nickel, P, and the B with the gestalt of mixture or a multiple oxide. Effectiveness is large, when an alumina is less than [more than 75wt%98wt%] and a titania is more than less than [25%] 2wt% with the catalyst containing especially an alumina and a titania.

Moreover, it is the oxide of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, nickel, P, and B to the amount of catalyst main 0.1 - 10wt% Effectiveness is large when it contains.

[0011] As a result of examining many things for development of the decomposition catalyst of fluorine compound content gas, it found out that it was necessary to contain the metal component which forms association of a fluorine and moderate strength as a property of a catalyst. In the case of the compound which consists of carbon and a fluorine especially, since the molecule itself was stable, the catalyst for which the fluoride enthalpy of formation contains a large metal component found out that superresolution activity was shown. If not much stable association is formed, in order that a fluorine compound may not separate from on a catalyst, activity falls gradually. On the other hand, if bonding strength is too weak, sufficient cracking severity will not be acquired. C2F6 which are object gas of this invention have the strong intramolecular force, and they are the reactant scarce matter. When burning these gas, the temperature of 1500-2000 degrees C is called need. Although it found out that it could decompose the gas for a book even if an alumina, a titania, a silica, and a zirconia are independently used for **** as a catalyst, as a catalyst which acquires higher cracking severity, the catalyst which comes to contain an alumina and a titania found out the desirable thing. It is thought that an alumina serves to draw a fluorine compound on a catalyst, and a titania serves to pull apart the fluorine compound on a catalyst.

[0012] The oxide of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, and nickel is regarded as making the concertante performance effectiveness with an alumina, a titania, a silica, and a zirconia discover. Moreover, it is thought that it has contributed to stabilization of the titania in a catalyst.

[0013] In the decomposition art of the fluorine compound content gas of this invention, it found out that fluorine compounds, such as C₂F₆, could be diluted with inert gas. By diluting the concentration of a fluorine compound, the load to a catalyst becomes small and decomposition activity can be maintained for a long time. As dilution gas, inert gas, such as Ar, N₂, and helium, can be used.

[0014] The fluorine content compound made into the object of this invention is called PFC(s) (perfluorocompound), such as C₂F₆ and NF₃, or FFC (fully fluorocompound), and has the following as a typical reaction.

[0015] It is desirable to add a hydrogen atom C₂F₆+3H₂ O->CO+CO₂+6HFC₂F₆+2H₂O+1/2O₂ ->2CO₂+6HFNF₃+3H₂ O->NO₂+1 / in the gas which processes the fluorine compound of these 2O₂+6 HF, so that it may become equivalent to the F number in a fluorine compound at least. By this, F in a compound turns into HF and F in a decomposition product becomes the gestalt of the hydrogen halide which is easy to carry out after treatment. As a source of hydrogen at this time, although hydrogen, a hydrocarbon, etc. can be used other than a steam, when a hydrocarbon is used, a hydrocarbon burns on a catalyst and can make small heat energy to supply.

[0016] Moreover, oxidation reaction of CO can also be made to occur simultaneously by making oxidation gas, such as oxygen, contain in reactant gas. When oxidation reaction of CO is imperfect, after removing HF in decomposition generation gas, CO oxidation catalyst is made to contact, and it is CO₂ about CO. It can also be made to convert.

[0017] if the catalyst of this invention is used -- chlorofluorocarbon-replacing materials, such as chlorofluocarbon, such as C₂Cl₃F₃, C₂Cl₂F₄, and C₂ClF₅, and HFC134a, and SF₆ etc. -- a compound can also be disassembled. Moreover, matter, such as CCl₃F and CCl₂F₂, can also be disassembled enough. In addition, Cl in the compound at the time of processing a chlorine compound is converted into HCl.

[0018] About 400 - 800 degrees C of abbreviation of the reaction temperature used by this invention are desirable. Degradation of a catalyst is quick, although the rate of superresolution will be obtained if it is used at the elevated temperature beyond this. Moreover, the corrosion rate of an equipment ingredient becomes large rapidly. On the contrary, at the temperature not more than this, cracking severity is low. Moreover, what carries out the spray of the alkali solution and washes it as a process which carries out neutralization clearance of the generated HF has high effectiveness, and since lock out of piping by crystal deposit etc. cannot take place easily, it is desirable. The approach of washing decomposition generation gas using the approach or packed column which carries out bubbling in an alkali solution may be used.

[0019] As an aluminum raw material for preparing the catalyst of this invention, the mixture of gamma-alumina, gamma-alumina, and delta alumina etc. can be used. A desirable approach also forms an oxide by final baking, especially using boehmite etc. as an aluminum raw material.

[0020] As a Ti raw material for preparing the catalyst of this invention, sulfuric-acid titanium, a titania sol, a titanium slurry, etc. can be used.

[0021] Furthermore, as a raw material of the third metal components, such as Si, Mg, and Zr, various kinds, a nitrate, ammonium salt, a chloride, etc. can be used.

[0022] The manufacturing method of the catalyst of this invention can use all, such as settling usually used for manufacture of a catalyst, an impregnation method, and the kneading method.

[0023] Moreover, the catalyst in this invention can be used, fabricating it a grain, in the shape of a honeycomb, etc. as it is. As a fabricating method, the approach of arbitration is [/ for the purpose of an extrusion-molding method, the making tablet fabricating method, the rolling corning method, etc.] employable. Moreover, it can also be used, being able to coat the honeycomb and plate made from a ceramic metallurgy group.

[0024] The fluorine compound content gassing approach of this invention can disassemble a fluorine compound at low temperature compared with other arts.

[0025] When processing fluorine compound content gas, the corrosion of the equipment ingredient by acid components, such as HF decomposed and generated, poses a problem, but since the temperature to be used is low temperature comparatively according to this invention, a corrosion rate is slow and the maintenance of equipment etc. becomes unnecessary.

[0026] The equipment which enforces the fluorine compound content gassing approach of this invention can miniaturize equipment that what is necessary is just to have the facility which carries out neutralization clearance of the acid component in the catalytic-reaction tub which disassembles a fluorine compound, and decomposition generation gas.

[0027]

[Embodiment of the Invention] Hereafter, an example explains this invention to a detail further. This invention is not limited only to these examples.

[0028] Drawing 1 shows the example in the case of using the decomposition art of this invention at the cleaning process of the plasma-CVD equipment of a semi-conductor production process.

[0029] Plasma-CVD equipment is SiO₂ to a semi-conductor wafer front face. It is equipment in which the film is made to form with vacuum deposition. However, SiO₂ The film is SiO₂ attached to the unnecessary part since it adhered in [whole] equipment. It is necessary to remove. This SiO₂ In order to clean, C₂F₆ are used. The cleaning gas containing C₂F₆ is sent to a CVD chamber, is excited with the plasma, and removes SiO₂. Then, the inside of a chamber is permuted by N₂, C₂F₆ concentration is diluted to about 3 - 5%, and they are about 15 l/min. It has discharged from the chamber.

[0030] Air 3 was added to this emission gas, and C₂F₆ were diluted. The reactant gas 5 which added the steam 4 further to this dilution gas is sent to a decomposition process. C₂F₆ concentration in reactant gas -- about 0.5% it is . In a decomposition process, reactant gas 5 is contacted at an aluminum₂O₃ system catalyst and 700 degrees C on condition that space-velocity 3000 per hour (space velocity (h⁻¹) = a reactant gas flow rate (ml/h) / the amount of catalysts (ml)). In this case, reactant gas may be heated and a catalyst may be heated with an electric furnace etc. Cracked gas 6 is sent to an exhaust gas washing process. At an exhaust gas washing process, the spray of the alkali water solution is carried out to cracked gas 6, and the exhaust gas 7 with which the acid component in cracked gas was removed is emitted out of a system. The cracking severity of C₂F₆ analyzes reactant gas 5 and exhaust gas 7 using a FID (abbreviated name of Flame Ionization Detector) gas chromatograph, and a TCD (abbreviated name of Thermal

Conductivity Detector) gas chromatograph, and asks for them by the material balance of an entry and an outlet.

[0031] Hereafter, the result of having investigated the activity of various fluorine compound decomposition catalysts is explained.

[0032] Air was added and diluted in C₂F₆ gas of 99% or more of [example 1] purity. To this dilution gas, the steam was added further. The steam supplied pure water to the coil upper part using the micro tube pump, and made it gasify by 0.11 ml/min. C₂F₆ concentration in reactant gas -- about 0.5% it was. It was made to contact in the catalyst and space-velocity 3000 per hour which warmed this reactant gas at 700 degrees C from the coil exterior with the electric furnace.

[0033] A coil is a coil with a bore of 19mm made from Inconel, has the catalyst bed in the center of a coil, and has the pyrometer tube with an outer diameter of 3mm made from Inconel inside. Bubbling of the decomposition generation gas which passed the catalyst bed was carried out into the sodium-hydroxide solution, and it was emitted out of the system. The cracking severity of C₂F₆ was searched for by the degree type by the FID gas chromatograph and the TCD gas chromatograph.

[0034]

[Equation 1]

$$\text{分解率} = 1 - \frac{\text{出口のフッ素化合物}}{\text{供給したフッ素化合物}} \times 100 \text{ (%)}$$

… (数1)

[0035] The method of preparation of each catalyst with which the trial in the above-mentioned conditions was presented is shown below.

[0036] The granular alumina (NKHD-24) by catalyst 1;aluminum₂O₃ Sumitomo Chemical is ground, and it is 0.5 to 1 mm. The trial was presented with what dried at a sieve part opium poppy and 120 degrees C to particle size for 2 hours, and was calcinated at 700 degrees C for 2 hours.

[0037] The granular titania (CS-200-24) made from catalyst 2;TiO₂ Sakai chemistry is ground, and it is 0.5 to 1 mm. The trial was presented with what dried at a sieve part opium poppy and 120 degrees C to particle size for 2 hours, and was calcinated at 700 degrees C for 2 hours.

[0038] 200g of catalyst 3;ZrO₂ zirconium nitrate was dried at 120 degrees C for 2 hours, and it calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. It corned to the zirconia of particle size and the trial was presented.

[0039] The trial was presented with what ground the granular silica (CARIAC-T-10) made from catalyst 4;SiO₂Fuji Silyria, dried at a sieve part opium poppy and 120 degrees C to 0.5-1mm particle size for 2 hours, and was calcinated at 700 degrees C for 2 hours.

[0040] a catalyst -- the granular titania (CS-200-24) made from 5;TiO₂-ZrO₂ Sakai chemistry -- 0.5mm It ground below. It is 78.3g of zirconium nitrate to 100g of this powder. In addition, it kneaded, adding pure water. It dried at 120 degrees C after kneading for 2 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. It corned to particle size and the trial was presented.

[0041] a catalyst -- the granular alumina (NKHD-24) by 6;aluminum2O3-MgO
Sumitomo Chemical -- 0.5mm It ground to the following particle size. It is 56.4g of magnesium nitrates to 100g of this powder. In addition, it kneaded, adding pure water. It dried at 120 degrees C after kneading for 2 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0042] a catalyst 7 -- the granular alumina (NKHD-24) by;aluminum2O3-TiO₂
Sumitomo Chemical -- 0.5mm It ground to the following particle size. It is 56.4g of desiccation powder of a metatitanic acid slurry to 100g of this powder. In addition, it kneaded, adding pure water. It dried at 120 degrees C after kneading for 2 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0043] a catalyst 8 -- the granular alumina (NKHD-24) by;aluminum2O3-SiO₂
Sumitomo Chemical -- 0.5mm It ground to the following particle size. It is SiO₂ to 100g of this powder. 13.2g of desiccation powder of a sol In addition, it kneaded, adding pure water. It dried at 120 degrees C after kneading for 2 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0044] The test result of the above-mentioned catalysts 1-8 is shown in drawing 2 .

[0045] [Example 2] this examples are the same conditions as an example 1, and investigate the effectiveness of third component addition. Each catalyst was prepared as follows.

[0046] a catalyst 9 -- the granular alumina (NKHD-24) by;aluminum2O3-TiO₂
Sumitomo Chemical -- grinding -- 0.5 to 1 mm It dried at a sieve part opium poppy and 120 degrees C to particle size for 2 hours. It sank into this in 176g of sulfuric-acid titanium solutions 30%. It dried at 250-300 degrees C after impregnation for about 5 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0047] catalyst 10;aluminum2 -- the granular alumina (NKHD-24) by O₃-TiO₂-ZrO₂
Sumitomo Chemical -- grinding -- 0.5 to 1 mm It dried at a sieve part opium poppy and 120 degrees C to particle size for 2 hours. It sank into this in 176g of sulfuric-acid titanium solutions 30%. It dried at 250-300 degrees C after impregnation for about 5 hours, and calcinated at 700 degrees C for 2 hours, and Catalyst A was produced. Then, the water solution which melted 6.7g of zirconium nitrate 2 hydrates to catalyst A50g at 90g H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0048] Catalyst A was produced by the same approach as the catalyst 11;aluminum2O₃-TiO₂-WO₃ catalyst 10. Then, the 90g water solution which melted Para tungstic-acid ammonium 6.5g to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0049] Catalyst A was produced by the same approach as the catalyst 12;aluminum2O₃-TiO₂-SiO₂ catalyst 10. Then, the 90g water solution which melted 20wt% silica sol 7.5g to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2

hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this. Catalyst A was produced by the same approach as the catalyst 13;aluminum2O3-TiO2-SnO2 catalyst 10. Then, the 90g water solution which melted 5.6g of chlorination tin 2 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0050] Catalyst A was produced by the same approach as the catalyst 14;aluminum2O3-TiO2-CeO2 catalyst 10. Then, the 90g water solution which melted 10.9g of cerium-nitrate 6 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

Catalyst A was produced by the same approach as the catalyst 15;aluminum2O3-TiO2-MnO2 catalyst 10. Then, the 90g water solution which melted 7.2g of manganese nitrate 6 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0051] Catalyst A was produced by the same approach as the catalyst 16;aluminum2O3-TiO2-Bi2O3 catalyst 10. Then, the 90g water solution which melted 7.4g of bismuth nitrate 6 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0052] Catalyst A was produced by the same approach as the catalyst 17;aluminum2O3-TiO2-NiO catalyst 10. Then, the 90g water solution which melted 7.3g of nickel nitrate 6 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0053] Catalyst A was produced by the same approach as the catalyst 18;aluminum2O3-TiO2-BO4 catalyst 10. Then, the 90g water solution which melted 12.0g of way acid ammonium 8 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0054] The activity of the above-mentioned catalysts 9-18 and the catalyst 1 in an example 1 is shown in drawing 3 .

[0055] [Example 3] this example changes an alumina raw material and a titania raw material, prepares various catalysts, and are an example 1 and an example which investigated activity by the same approach.

[0056] The boehmite powder made from catalyst 19;aluminum2O3CONDEA (PURAL SB) was dried at 120 degrees C for 2 hours. It is 0.5 at 300 degrees C in 200g of this desiccation powder. Time amount baking was carried out, and further, burning temperature was raised to 700 degrees C, and was calcinated for 2 hours. The obtained powder was put into metal mold and compression molding was carried out by the pressure of 500 kgf/cm². A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0057] a catalyst 20 -- the boehmite powder made from;aluminum2O3-TiO2CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. 200g of this desiccation powder, 248.4g of 30% sulfuric-acid titanium solutions It kneaded adding about 200g of pure

water. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0058] a catalyst 21 -- the boehmite powder made from;aluminum2O3-TiO2CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. 200g of this desiccation powder, and 30% titania sol 78.6g About 100g water solution which added pure water was kneaded. It dried at 120 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm².

Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The result of having investigated the activity of the above-mentioned catalysts 19-21 by the same approach as an example 1 is shown in drawing 4 .

[0059] [Example 4] this example is the result of preparing the catalyst to which the presentation of aluminum and Ti in the catalyst 20 of an example 3 was changed, and investigating activity.

[0060] a catalyst 22 -- the boehmite powder made from;aluminum2O3-TiO2CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. 100g of this desiccation powder, 48.8g of 30% sulfuric-acid titanium solutions It kneaded adding about 150g of pure water. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0061] a catalyst 23 -- the boehmite powder made from;aluminum2O3-TiO2CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. 100g of this desiccation powder, 82.4g of 30% sulfuric-acid titanium solutions It kneaded adding about 120g of pure water. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0062] a catalyst 24 -- the boehmite powder made from;aluminum2O3-TiO2CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. 100g of this desiccation powder, 174.4g of 30% sulfuric-acid titanium solutions It kneaded adding about 70g of pure water. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0063] a catalyst 25 -- the boehmite powder made from;aluminum2O3-TiO2CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. It kneaded adding 100g of this desiccation powder, and 392g of 30% sulfuric-acid titanium solutions. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0064] The result of having investigated the activity of the above-mentioned catalysts 22-25 by the same approach as an example 1 is shown in drawing 5 .

[0065] [Example 5] this example is an example at the time of adding a sulfuric acid at the time of catalyst preparation.

[0066] a catalyst 26 -- the boehmite powder made from;aluminum2O3-TiO2CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. In 150g of this desiccation powder, it is 58.8g of Ishihara Sangyo CS-N30% titania sol solutions. 44.8g of 97% sulfuric-acid solutions The water solution diluted with 250ml of pure water was added and kneaded. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The test condition is the same as an example 1 except having made space velocity into 1000 per hour. 80% of cracking severity of C₂F₆ was acquired with the reaction temperature of 650 degrees C as a result of the trial.

[0067]

[Effect of the Invention] according to this invention -- C₂F₆ and NF₃ etc. -- decomposition processing of the fluorine content gas can be carried out efficiently.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the decomposition art and catalyst ingredient which decompose efficiently fluorine compound content gas, such as C₂F₆, at low temperature.

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PRIOR ART

[Description of the Prior Art] Fluorine compound gas, such as C₂F₆, is used by the large quantity for a semi-conductor etching ingredient and semi-conductor washing. However, if these matter is emitted into atmospheric air, it has turned out that it is the quality of a warm ghost which causes warming of the earth. From now on, it will be expected to the processing after the activity of these compounds that severe regulation is performed.

[0003] By the way, gas, such as C₂F₆, contains many fluorines (F) as a molecule constituent. Electronegativity of a fluorine is the largest of all elements, and it forms the chemical very stable matter. C₂F₆ etc. have the especially strong intramolecular force, and it is the matter lacking in reactivity. From this property, an elevated temperature is required to decompose and the energy of a large quantity is consumed. Moreover, the decomposition reaction in an elevated temperature has the large corrosion rate of the equipment ingredient by gas, such as hydrogen fluoride to generate, and the actual condition is that there is no suitable decomposition art.

[0004] As a decomposition art, current and being proposed are the combustion technologies in an elevated temperature. However, by this approach, in order to use the fuel of a large quantity, energy efficiency is low and the problem of breakage on the furnace wall by the halogenated compound 1000 degrees C or more generated with combustion also has it. Therefore, the technique which can be decomposed more at low temperature is required.

[0005] About the catalyst, TiO₂-WO₃ catalyst is reported to JP,6-59388,B as a catalyst for decomposition of an organic halogenated compound until now. This catalyst is 0.1 - 20wt% of TiO₂. It is a catalyst (when it is made an atomic ratio, Ti is 99.96% or less 92% or more, and W is 0.04% or more 8% or less) containing W, and although CCl₄ of ppm order is processed, 99% of cracking severity was held at 375 degrees C for 1500 hours. Not only Cl but the F of the effect as catalyst poison is larger rather in an organic halogenated compound. With this official report, it is the organic halogenated compound 4 of a carbon number 1, i.e., CF. Although Cl₂F₂ grade can be decomposed, there is no example of the decomposition result about a fluorine compound. Moreover, generally compared with disassembly of the organic halogenated compound of a carbon number 1, it is hard to disassemble the organic halogenated compound of a carbon number 2. As another example, aluminum₂O₃-ZrO₂-WO₃ catalyst is reported to JP,7-80303,A as a decomposition catalyst of fluorine compound gas. This catalyst is a catalyst which understands chlorofluocarbon a burned part, carried out the combustion decomposition reaction to processing chlorofluocarbon -115 (C₂ClF₅) at 600 degrees C, and held 98% of cracking severity for 10 hours. Processing cost becomes large in order that this approach may add hydrocarbons, such as n-butane, as a combustion assistant. Moreover, although disassembly of the compound of only the carbon of C₂F₆ grade and a fluorine is still more difficult compared with chlorofluocarbon -115, there is no example of the decomposition result about these matter.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] according to this invention -- C2F6 and NF3 etc. --
decomposition processing of the fluorine content gas can be carried out efficiently.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The object of this invention offers the approach and catalyst which carry out decomposition processing of the gas containing either [at least] the compound containing a fluorine atom, or the compound containing a nitrogen atom and a fluorine atom efficiently at low temperature including two or more carbon.

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MEANS

[Means for Solving the Problem] this invention persons were low temperature, and could be efficient, could decompose fluorine compound content gas, and as a result of advancing examination of the decomposition art which corrosion of the equipment by the hydrogen fluoride which moreover separates as a decomposition product cannot produce easily to a detail, they resulted in this invention.

[0008] That is, it found out that the fluorine in a gas stream could be converted into HF by contacting the gas stream containing either [at least] the compound containing a fluorine atom, or the compound containing a nitrogen atom and a fluorine atom under existence of the steam of an effective dose at a specific fluorine compound decomposition catalyst and the temperature of about 400 - 800 degrees C of abbreviation, including two or more carbon. As a decomposition catalyst, the catalyst of an alumina, a titania, a silica, and a zirconia which contains a kind at least can be used.

[0009] as a fluorine compound -- C₂F₆ etc. -- like -- a carbon number -- two or more compounds of C and F, and NF₃ etc. -- there is a compound of N and F etc.

[0010] Furthermore, when at least 1 component of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, and the nickel was added for the catalyst, it found out that fluorine compound content gas could be decomposed in higher activity. These catalysts contain the oxide of an alumina, a titania, a silica, a zirconia, and at least 1 component of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, nickel, P, and the B with the gestalt of mixture or a multiple oxide. Effectiveness is large, when an alumina is less than [more than 75wt%98wt%] and a titania is more than less than [25%] 2wt% with the catalyst containing especially an alumina and a titania.

Moreover, it is the oxide of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, nickel, P, and B to the amount of catalyst main 0.1 - 10wt% Effectiveness is large when it contains.

[0011] As a result of examining many things for development of the decomposition catalyst of fluorine compound content gas, it found out that it was necessary to contain the metal component which forms association of a fluorine and moderate strength as a property of a catalyst. In the case of the compound which consists of carbon and a fluorine especially, since the molecule itself was stable, the catalyst for which the fluoride enthalpy of formation contains a large metal component found out that superresolution activity was shown. If not much stable association is formed, in order that a fluorine compound may not separate from on a catalyst, activity falls gradually. On the other hand, if bonding strength is too weak, sufficient cracking severity will not be acquired. C₂F₆ which are object gas of this invention have the strong intramolecular force, and they are the reactant scarce matter. When burning these gas, the temperature of 1500-2000 degrees C is called need. Although it found out that it could decompose the gas for a book even if an alumina, a titania, a silica, and a zirconia are independently used for **** as a catalyst, as a catalyst which acquires higher cracking severity, the catalyst which comes to contain an alumina and a titania found out the desirable thing. It is thought that an alumina serves to draw a fluorine compound on a catalyst, and a titania serves to pull apart the fluorine compound on a catalyst.

[0012] The oxide of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, and nickel is regarded as making the concertante performance effectiveness with an alumina, a titania, a silica, and a zirconia discover. Moreover, it is thought that it has contributed to stabilization of the titania in a catalyst.

[0013] In the decomposition art of the fluorine compound content gas of this invention, it found out that fluorine compounds, such as C₂F₆, could be diluted with inert gas. By

diluting the concentration of a fluorine compound, the load to a catalyst becomes small and decomposition activity can be maintained for a long time. As dilution gas, inert gas, such as Ar, N₂, and helium, can be used.

[0014] The fluorine content compound made into the object of this invention is called PFC(s) (perfluorocompound), such as C₂F₆ and NF₃, or FFC (fully fluorocompound), and has the following as a typical reaction.

[0015] It is desirable to add a hydrogen atom C₂F₆+3H₂ O->CO+CO₂+6HFC₂F₆+2H₂O+1/2O₂ ->2CO₂+6HFNF₃+3H₂ O->NO₂+1 / in the gas which processes the fluorine compound of these 2O₂+6 HF, so that it may become equivalent to the F number in a fluorine compound at least. By this, F in a compound turns into HF and F in a decomposition product becomes the gestalt of the hydrogen halide which is easy to carry out after treatment. As a source of hydrogen at this time, although hydrogen, a hydrocarbon, etc. can be used other than a steam, when a hydrocarbon is used, a hydrocarbon burns on a catalyst and can make small heat energy to supply.

[0016] Moreover, oxidation reaction of CO can also be made to occur simultaneously by making oxidation gas, such as oxygen, contain in reactant gas. When oxidation reaction of CO is imperfect, after removing HF in decomposition generation gas, CO oxidation catalyst is made to contact, and it is CO₂ about CO. It can also be made to convert.

[0017] if the catalyst of this invention is used -- chlorofluorocarbon-replacing materials, such as chlorofluocarbon, such as C₂Cl₃F₃, C₂Cl₂F₄, and C₂ClF₅, and HFC134a, and SF₆ etc. -- a compound can also be disassembled. Moreover, matter, such as CCl₃F and CCl₂F₂, can also be disassembled enough. In addition, Cl in the compound at the time of processing a chlorine compound is converted into HCl.

[0018] About 400 - 800 degrees C of abbreviation of the reaction temperature used by this invention are desirable. Degradation of a catalyst is quick, although the rate of superresolution will be obtained if it is used at the elevated temperature beyond this. Moreover, the corrosion rate of an equipment ingredient becomes large rapidly. On the contrary, at the temperature not more than this, cracking severity is low. Moreover, what carries out the spray of the alkali solution and washes it as a process which carries out neutralization clearance of the generated HF has high effectiveness, and since lock out of piping by crystal deposit etc. cannot take place easily, it is desirable. The approach of washing decomposition generation gas using the approach or packed column which carries out bubbling in an alkali solution may be used.

[0019] As an aluminum raw material for preparing the catalyst of this invention, the mixture of gamma-alumina, gamma-alumina, and delta alumina etc. can be used. A desirable approach also forms an oxide by final baking, especially using boehmite etc. as an aluminum raw material.

[0020] As a Ti raw material for preparing the catalyst of this invention, sulfuric-acid titanium, a titania sol, a titanium slurry, etc. can be used.

[0021] Furthermore, as a raw material of the third metal components, such as Si, Mg, and Zr, various kinds, a nitrate, ammonium salt, a chloride, etc. can be used.

[0022] The manufacturing method of the catalyst of this invention can use all, such as settling usually used for manufacture of a catalyst, an impregnation method, and the kneading method.

[0023] Moreover, the catalyst in this invention can be used, fabricating it a grain, in the

shape of a honeycomb, etc. as it is. As a fabricating method, the approach of arbitration is [/ for the purpose of an extrusion-molding method, the making tablet fabricating method, the rolling corning method, etc.] employable. Moreover, it can also be used, being able to coat the honeycomb and plate made from a ceramic metallurgy group.

[0024] The fluorine compound content gassing approach of this invention can disassemble a fluorine compound at low temperature compared with other arts.

[0025] When processing fluorine compound content gas, the corrosion of the equipment ingredient by acid components, such as HF decomposed and generated, poses a problem, but since the temperature to be used is low temperature comparatively according to this invention, a corrosion rate is slow and the maintenance of equipment etc. becomes unnecessary.

[0026] The equipment which enforces the fluorine compound content gassing approach of this invention can miniaturize equipment that what is necessary is just to have the facility which carries out neutralization clearance of the acid component in the catalytic-reaction tub which disassembles a fluorine compound, and decomposition generation gas.

[0027]

[Embodiment of the Invention] Hereafter, an example explains this invention to a detail further. This invention is not limited only to these examples.

[0028] Drawing 1 shows the example in the case of using the decomposition art of this invention at the cleaning process of the plasma-CVD equipment of a semi-conductor production process.

[0029] Plasma-CVD equipment is SiO₂ to a semi-conductor wafer front face. It is equipment in which the film is made to form with vacuum deposition. However, SiO₂ The film is SiO₂ attached to the unnecessary part since it adhered in [whole] equipment. It is necessary to remove. This SiO₂ In order to clean, C₂F₆ are used. The cleaning gas containing C₂F₆ is sent to a CVD chamber, is excited with the plasma, and removes SiO₂. Then, the inside of a chamber is permuted by N₂, C₂F₆ concentration is diluted to about 3 - 5%, and they are about 15 l/min. It has discharged from the chamber.

[0030] Air 3 was added to this emission gas, and C₂F₆ were diluted. The reactant gas 5 which added the steam 4 further to this dilution gas is sent to a decomposition process. C₂F₆ concentration in reactant gas -- about 0.5% it is . In a decomposition process, reactant gas 5 is contacted at an aluminum₂O₃ system catalyst and 700 degrees C on condition that space-velocity 3000 per hour (space velocity (h⁻¹) = a reactant gas flow rate (ml/h) / the amount of catalysts (ml)). In this case, reactant gas may be heated and a catalyst may be heated with an electric furnace etc. Cracked gas 6 is sent to an exhaust gas washing process. At an exhaust gas washing process, the spray of the alkali water solution is carried out to cracked gas 6, and the exhaust gas 7 with which the acid component in cracked gas was removed is emitted out of a system. The cracking severity of C₂F₆ analyzes reactant gas 5 and exhaust gas 7 using a FID (abbreviated name of Flame Ionization Detector) gas chromatograph, and a TCD (abbreviated name of Thermal Conductivity Detector) gas chromatograph, and asks for them by the material balance of an entry and an outlet.

[0031] Hereafter, the result of having investigated the activity of various fluorine compound decomposition catalysts is explained.

[0032] Air was added and diluted in C₂F₆ gas of 99% or more of [example 1] purity. To this dilution gas, the steam was added further. The steam supplied pure water to the coil

upper part using the micro tube pump, and made it gasify by 0.11 ml/min. C2F6 concentration in reactant gas -- about 0.5% it was . It was made to contact in the catalyst and space-velocity 3000 per hour which warmed this reactant gas at 700 degrees C from the coil exterior with the electric furnace.

[0033] A coil is a coil with a bore of 19mm made from Inconel, has the catalyst bed in the center of a coil, and has the pyrometer tube with an outer diameter of 3mm made from Inconel inside. Bubbling of the decomposition generation gas which passed the catalyst bed was carried out into the sodium-hydroxide solution, and it was emitted out of the system. The cracking severity of C2F6 was searched for by the degree type by the FID gas chromatograph and the TCD gas chromatograph.

[0034]

[Equation 1]

$$\text{分解率} = 1 - \frac{\text{出口のフッ素化合物}}{\text{供給したフッ素化合物}} \times 100 \text{ (%)}$$

… (数1)

[0035] The method of preparation of each catalyst with which the trial in the above-mentioned conditions was presented is shown below.

[0036] The granular alumina (NKHD-24) by catalyst 1;aluminum2O3 Sumitomo Chemical is ground, and it is 0.5 to 1 mm. The trial was presented with what dried at a sieve part opium poppy and 120 degrees C to particle size for 2 hours, and was calcinated at 700 degrees C for 2 hours.

[0037] The granular titania (CS-200-24) made from catalyst 2;TiO2 Sakai chemistry is ground, and it is 0.5 to 1 mm. The trial was presented with what dried at a sieve part opium poppy and 120 degrees C to particle size for 2 hours, and was calcinated at 700 degrees C for 2 hours.

[0038] 200g of catalyst 3;ZrO2 zirconium nitrate was dried at 120 degrees C for 2 hours, and it calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm2. Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. It corned to the zirconia of particle size and the trial was presented.

[0039] The trial was presented with what ground the granular silica (CARIAC-T-10) made from catalyst 4;SiO2Fuji Silysia, dried at a sieve part opium poppy and 120 degrees C to 0.5-1mm particle size for 2 hours, and was calcinated at 700 degrees C for 2 hours.

[0040] a catalyst -- the granular titania (CS-200-24) made from 5;TiO2-ZrO2 Sakai chemistry -- 0.5mm It ground below. It is 78.3g of zirconium nitrate to 100g of this powder. In addition, it kneaded, adding pure water. It dried at 120 degrees C after kneading for 2 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm2. Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. It corned to particle size and the trial was presented.

[0041] a catalyst -- the granular alumina (NKHD-24) by 6;aluminum2O3-MgO Sumitomo Chemical -- 0.5mm It ground to the following particle size. It is 56.4g of magnesium nitrates to 100g of this powder. In addition, it kneaded, adding pure water. It dried at 120 degrees C after kneading for 2 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm2. Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1

mm. The trial was presented as a particle size.

[0042] a catalyst 7 -- the granular alumina (NKHD-24) by;aluminum₂O₃-TiO₂ Sumitomo Chemical -- 0.5mm It ground to the following particle size. It is 56.4g of desiccation powder of a metatitanic acid slurry to 100g of this powder. In addition, it kneaded, adding pure water. It dried at 120 degrees C after kneading for 2 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0043] a catalyst 8 -- the granular alumina (NKHD-24) by;aluminum₂O₃-SiO₂ Sumitomo Chemical -- 0.5mm It ground to the following particle size. It is SiO₂ to 100g of this powder. 13.2g of desiccation powder of a sol In addition, it kneaded, adding pure water. It dried at 120 degrees C after kneading for 2 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm².

Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0044] The test result of the above-mentioned catalysts 1-8 is shown in drawing 2 .

[0045] [Example 2] this examples are the same conditions as an example 1, and investigate the effectiveness of third component addition. Each catalyst was prepared as follows.

[0046] a catalyst 9 -- the granular alumina (NKHD-24) by;aluminum₂O₃-TiO₂ Sumitomo Chemical -- grinding -- 0.5 to 1 mm It dried at a sieve part opium poppy and 120 degrees C to particle size for 2 hours. It sank into this in 176g of sulfuric-acid titanium solutions 30%. It dried at 250-300 degrees C after impregnation for about 5 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0047] catalyst 10;aluminum₂ -- the granular alumina (NKHD-24) by O₃-TiO₂-ZrO₂ Sumitomo Chemical -- grinding -- 0.5 to 1 mm It dried at a sieve part opium poppy and 120 degrees C to particle size for 2 hours. It sank into this in 176g of sulfuric-acid titanium solutions 30%. It dried at 250-300 degrees C after impregnation for about 5 hours, and calcinated at 700 degrees C for 2 hours, and Catalyst A was produced. Then, the water solution which melted 6.7g of zirconium nitrate 2 hydrates to catalyst A50g at 90g H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0048] Catalyst A was produced by the same approach as the catalyst 11;aluminum₂O₃-TiO₂-WO₃ catalyst 10. Then, the 90g water solution which melted Para tungstic-acid ammonium 6.5g to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0049] Catalyst A was produced by the same approach as the catalyst 12;aluminum₂O₃-TiO₂-SiO₂ catalyst 10. Then, the 90g water solution which melted 20wt% silica sol 7.5g to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this. Catalyst A was produced by the same approach as the catalyst 13;aluminum₂O₃-TiO₂-SnO₂ catalyst 10. Then, the 90g water solution which melted 5.6g of chlorination tin 2 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0050] Catalyst A was produced by the same approach as the catalyst 14;aluminum2O3-TiO2-CeO2 catalyst 10. Then, the 90g water solution which melted 10.9g of cerium-nitrate 6 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

Catalyst A was produced by the same approach as the catalyst 15;aluminum2O3-TiO2-MnO₂ catalyst 10. Then, the 90g water solution which melted 7.2g of manganese nitrate 6 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0051] Catalyst A was produced by the same approach as the catalyst 16;aluminum2O3-TiO2-Bi2O3 catalyst 10. Then, the 90g water solution which melted 7.4g of bismuth nitrate 6 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0052] Catalyst A was produced by the same approach as the catalyst 17;aluminum2O3-TiO2-NiO catalyst 10. Then, the 90g water solution which melted 7.3g of nickel nitrate 6 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0053] Catalyst A was produced by the same approach as the catalyst 18;aluminum2O3-TiO2-BO₄ catalyst 10. Then, the 90g water solution which melted 12.0g of way acid ammonium 8 hydrates to catalyst A50g at H₂O was sunk in. It dried at 120 degrees C after impregnation for 2 hours, and calcinated at 700 degrees C for 2 hours. The trial was presented with this.

[0054] The activity of the above-mentioned catalysts 9-18 and the catalyst 1 in an example 1 is shown in drawing 3 .

[0055] [Example 3] this example changes an alumina raw material and a titania raw material, prepares various catalysts, and are an example 1 and an example which investigated activity by the same approach.

[0056] The boehmite powder made from catalyst 19;aluminum2O3CONDEA (PURAL SB) was dried at 120 degrees C for 2 hours. It is 0.5 at 300 degrees C in 200g of this desiccation powder. Time amount baking was carried out, and further, burning temperature was raised to 700 degrees C, and was calcinated for 2 hours. The obtained powder was put into metal mold and compression molding was carried out by the pressure of 500 kgf/cm². A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0057] a catalyst 20 -- the boehmite powder made from;aluminum2O3-TiO2CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. 200g of this desiccation powder, 248.4g of 30% sulfuric-acid titanium solutions It kneaded adding about 200g of pure water. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0058] a catalyst 21 -- the boehmite powder made from;aluminum2O3-TiO2CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. 200g of this desiccation powder, and

30% titania sol 78.6g About 100g water solution which added pure water was kneaded. It dried at 120 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm².

Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The result of having investigated the activity of the above-mentioned catalysts 19-21 by the same approach as an example 1 is shown in drawing 4.

[0059] [Example 4] this example is the result of preparing the catalyst to which the presentation of aluminum and Ti in the catalyst 20 of an example 3 was changed, and investigating activity.

[0060] a catalyst 22 -- the boehmite powder made from;aluminum₂O₃-TiO₂CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. 100g of this desiccation powder, 48.8g of 30% sulfuric-acid titanium solutions It kneaded adding about 150g of pure water. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0061] a catalyst 23 -- the boehmite powder made from;aluminum₂O₃-TiO₂CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. 100g of this desiccation powder, 82.4g of 30% sulfuric-acid titanium solutions It kneaded adding about 120g of pure water. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0062] a catalyst 24 -- the boehmite powder made from;aluminum₂O₃-TiO₂CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. 100g of this desiccation powder, 174.4g of 30% sulfuric-acid titanium solutions It kneaded adding about 70g of pure water. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0063] a catalyst 25 -- the boehmite powder made from;aluminum₂O₃-TiO₂CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. It kneaded adding 100g of this desiccation powder, and 392g of 30% sulfuric-acid titanium solutions. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size.

[0064] The result of having investigated the activity of the above-mentioned catalysts 22-25 by the same approach as an example 1 is shown in drawing 5.

[0065] [Example 5] this example is an example at the time of adding a sulfuric acid at the time of catalyst preparation.

[0066] a catalyst 26 -- the boehmite powder made from;aluminum₂O₃-TiO₂CONDEA (PURAL SB) was dried at 120 degrees C for 1 hour. In 150g of this desiccation powder, it is 58.8g of Ishihara Sangyo CS-N30% titania sol solutions. 44.8g of 97% sulfuric-acid solutions The water solution diluted with 250ml of pure water was added and kneaded. It

dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. The obtained powder is put into metal mold and it is 500 kgf/cm². Compression molding was carried out by the pressure. A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The test condition is the same as an example 1 except having made space velocity into 1000 per hour. 80% of cracking severity of C₂F₆ was acquired with the reaction temperature of 650 degrees C as a result of the trial.

[Translation done.]

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3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is process drawing showing the treatment process by one example of this invention.

[Drawing 2] It is the graph which shows the engine performance of various fluorine compound decomposition catalysts.

[Drawing 3] It is the graph which shows the engine performance of various fluorine compound decomposition catalysts.

[Drawing 4] It is the graph which shows the engine performance of various fluorine compound decomposition catalysts.

[Drawing 5] It is the graph which shows the engine performance of various fluorine compound decomposition catalysts.

[Description of Notations]

1 [-- Reactant gas, 6 / -- Cracked gas, 7 / -- Exhaust gas.] -- C₂F₆ and 2 -- N₂, 3 -- Air, 4 -- A steam, 5

[Translation done.]

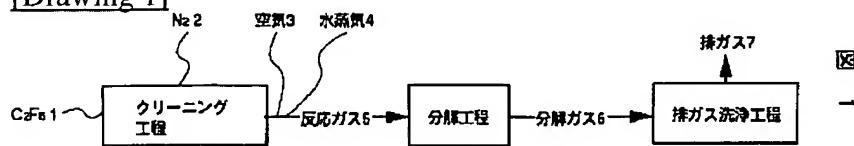
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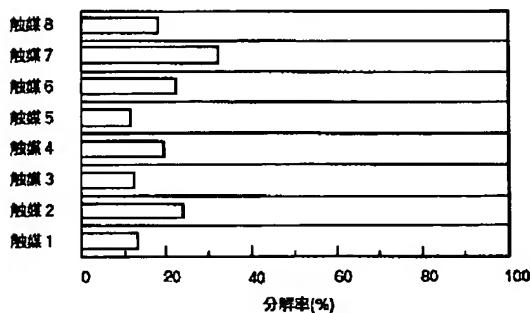
DRAWINGS

[Drawing 1]



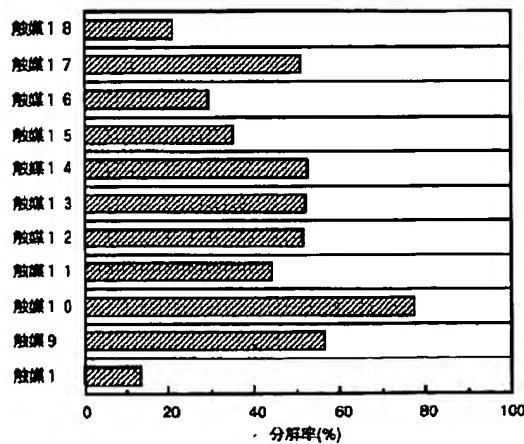
[Drawing 2]

図 2



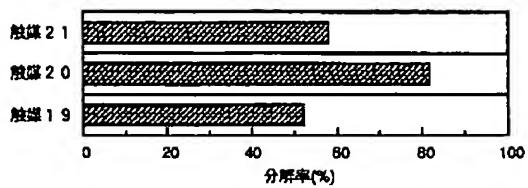
[Drawing 3]

図 3



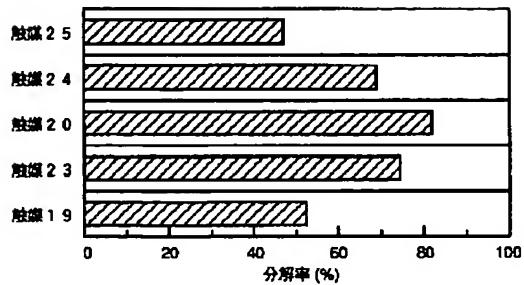
[Drawing 4]

図 4



[Drawing 5]

図 5



[Translation done.]